FABRICATION OF CHITOSAN AND POLY (VINYL ALCOHOL) BLEND MEMBRANES WITH DIFFERENT CONCENTRATION OF CHITOSAN

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I declare that this thesis entitled "*Fabrication of Chitosan and Poly (Vinyl Alcohol) Blend Membranes with Different Concentration of Chitosan*" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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"To my beloved mother, late father, family and someone special who gave me encouragement and support towards this study"

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ABSTRACT

Nowadays, the technology of membrane has become famous and widely used in the world. Many types of membrane have been invented including the chitosan (CS) membrane and also the poly (vinyl alcohol) (PVA) membrane. The objectives of this research are to fabricate the blend membrane using of chitosan and PVA with different concentration of chitosan, to study the performances and the morphology changes of each membrane. In this study, chitosan was blended with PVA to get the flat sheet blend membranes. PVA was used as the polymer matrix and CS as the functional polymer to provide amine group for the flat sheet blend membrane in order to make it adsorptive. There are two types of CS/PVA blend membrane which are Blend I (2.5wt% of CS) and Blend II (3.0wt% of CS). Acetic acid was used as a solvent for CS and PVA in preparing the dope solution. Formaldehyde and H_2SO_4 was used to form crosslinking between PVA and chitosan. NaOH solution was used as both the external and internal coagulants. These membranes were being tested on pure water permeability (PWP), rejection (R), flux rate (J) and also the morphologies changes in each membrane. The adsorption performance of the flat sheet blend membrane was evaluated through the adsorption of BSA solution and lysozime. The results reveal that, PWP was increased by increasing of concentration of CS. Besides, the pores size was increase when the concentration of CS was increased. The rejection and also the flux rate also increase by increasing the concentration of CS. In a nut shell, different concentration of CS enhanced the performances and the morphologies of the membrane.

ABSTRAK

Dewasa ini, teknologi membran telah menjadi terkenal dan digunakan secara meluas di seluruh dunia. Terdapat pelabagai jenis membran yang telah dicipta membran chitosan (CS) dan juga membran poli (vinil alkohol) (PVA). Objektif kajian ini adalah untuk menghasilkan membran kisaran daripada CS dan PVA dengan menggunakan kepekatatan CS yang berbeza, mengkaji pencapaian dan perubahan morfologi bagi setiap membran. Dalam penyelidikan ini, CS dikisar besama PVA bagi mendapatkan kepingan membran yang nipis. PVA digunakan sebagai matrik polimer, manakala CS pula digunakan sebagai polimer berfungsi untuk membekalkan kumpulan amina supaya membran itu menjadi lebih terjerap. Terdapat dua jenis membrane kisaran yang dihasilkan dalam kajian ini iaitu Kisaran 1 (2.5wt% CS) dan Kisaran II (3.0wt%). Asid asetik digunakan sebagai pelarut CS dan PVA semasa penyediaan larutan membran. Formaldehid dan asid sulfurik dugunakan sebagai penjalin antara chitosan dan PVA. NaOH pula digunakan sebagai pengumpal bahagian dalam dan luar membran. Membran ini akan diuji dari segi Penelapan Air Tulen (PWP), Pemisahan Zat Terlarut (R), Kadar Pengaliran (*J*) dan juga perubahan morfologi bagi setiap membran. Kadar penjerapan membran akan diuji menggunakan bovine serum albumin(BSA) dan juga lisozim. Hasil kajian mendapati, PWP meningkat apabila kepekatan chitosan meningkat. Selain itu, saiz liang adalah semakin besar dengan peningkatan kepekatan chitosan. Pemisahan Zat Terlarut dan Kadar Pengaliran turut meningkat dengan pertambahn kepekatan chitosan. Kesimpulannya, perubahan chitosan memberi kesan kapada kadar pencapaian membrane dan juga morfologi membran.

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LIST OF SYMBOLS

$Å$	-	Angstrom(10^{-10})
A	-	Surface area(m^2)
C	-	concentratation
C_f	-	Concentration of feed stream
C_p	-	Solute concentration in permeate stream
E	-	energy
J	-	Flux rate
kPa	-	kilo Pascal
kV	-	kilovolt
MPa	-	megaPascal
nN	-	nanometer
P	-	pressure
Q	-	Volume of permeation(l)
R	-	Rejection
T	-	temperature
V	-	Volume of permeate(L)
$w/w\%$	-	Weight per weight percent
$<$	-	Less than
μm	-	Micrometer(10^{-6})

LIST OF ABBREVIATION

AFM	-	Atomic force microscopy
BSA	-	Bovine serum albumin
CA	-	Cellulose acetate
CS	-	Chitosan
DA	-	Degree of acetylation
ED	-	Electrodialysis
GS	-	Gas Separation
NaOH	-	Sodium hydroxide
NF		Nanofiltration
PES	-	Polyethersulfone
PS	-	Polysulfone
PVDF	-	Polyvinylidene difloride
SEM	-	Scanning electron microscope
UF	-	Ultrafiltration-

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Microfiltration membrane with surface functional group that can be used as coupling sites or adsorptive sites for the separation are of great interest in industrial and environmental application. Many commercial polymeric membrane materials such as polysulfone (PS), polyethersulfone (PES), polyvinylidene difloride (PVDF), polypropylene (PP) and nylon have good chemical, thermal and mechanical stability (Chinxiu *et al,* 2005). However, they are usually lack of reactive functional group on the polymer backbones. Hence membrane fabricated from these material have to be modified to eliminate the non-specific type of absorption and to enhance the separation efficiency through improved adsorptive surfaces, especially for biomolecules such as protein (Chinxiu *et al,* 2005).

In the last five decades, most studies of phase inversion mechanisms, ultra-thin skin layer formation and membrane morphology and pores size control were based on flat sheet or single layer asymmetric membranes (Nunes and Peinemann, 2001). Asymmetric membrane is characterized by a thin and dense skin layer on top of a porous substructure. It is well known that the skin layer provides major resistance to the permeation of solute through the membrane, whereas the porous substructure functions exclusively as a mechanical support. The capability of an asymmetric membrane to reject or admit a certain solute species is determined by the morphology, pore size and density of the skin layer (Nicholas, 1998). In order to control the membrane structure, low molecular weight component or the secondary

polymer is frequently used as the additive in the membrane forming system because it offers a convenient and effective way to develop high performance membranes (Ismail, 2006).

Chitosan is one of the promising membrane materials and has been widely studied. It can be used as membrane material for ultrafiltration, reverse osmosis, pervaporation and other kind of applications (Yuan *et al*, 1998). There has been considerable research interest to prepare chitosan membrane in flat sheet for adsorptive separation purpose, including the removal heavy metal ions. Recently, blending chitosan with other polymers has been found to be an effective way to overcome the shortcomings of chitosan (Liu and R Bai, 2006).

Since most commercially available membranes are synthesized or relatively inert material, the frequently used method to prepare affinity or adsorptive membrane is through surface modification of the commercial membranes (Koyano *et al,* 1999). In general, such system to prepare adsorptive membrane is complicated. An alternative method to prepare adsorptive membranes is to fabricate the membrane from a polymer or polymers blend which have reactive or functional group on the polymer backbone (Liu and R Bai, 2006).

1.2 Problem Statement

Membranes are increasingly playing on significant role in chemical technology and being used in variety of applications in our daily life. In membrane technology industries, the main problem in membrane technology is hard to get the performance with both high selectivity and flux flow rate. (Liu and Bai, 2006). This is because, most membranes selectivity are inversely proportional with flux flow rate. And the worst problem is serious fouling caused by the adsorption and deposition of biomacromolecules on the membrane surface and or inside the membrane pores which limits its efficient and wide application (Cailing *et al*, 2007).

Fouling is an irreversible process caused by solute adsorption and pore blocking, which can be minimized by using more hydrophilic membranes (Koyano *et al*, 1999). Therefore, hydrophilic membranes, such as PVA membrane, have become the preferential choice to resist protein fouling. Poly (vinyl alcohol) (PVA), with a highly hydrophilic character, good film-forming properties, outstanding physical and chemical stability is a kind of excellent membrane material for preparation of a hydrophilic membrane (Ying Shang *et al*, 2006). PVA is highly hydrophilic, non toxic and biocompatible polymer with excellent film forming properties, high mechanical strength, low fouling potential and long-term temperature and strong pH stability (Chunjin *et al*, 2007).

In order to control the membrane structure, low molecular weight component or the secondary polymer is frequently used as the additive in the membrane forming system because it offers a convenient and effective way to develop high performance membranes. It has been well known that the membrane morphology can be controlled by the addition of a small amount of additive (Ismail, 2006). Therefore, PVA is used in this experiment as an additive.

There are many researches that interest in using biopolymer chitosan to prepare adsorptive membrane. The high content of amine group in chitosan can serve as the reactive site that is available directly for adsorption separation application. Although pure and composite chitosan flat sheet membrane has been fabricated, these membranes are relatively less attractive for adsorption separation due to their small specific surface area (Wei *et al*, 2007).

To overcome these problems, some researcher has introduced some method that can improve the membrane performance. Yong Tang and friends have studied about the blending method by using chitosan and cellulose acetate. Blending and/or formation of composites is one of the attractive means of tuning the performance of a membrane to achieve the desired flux and/or selectivity (Dubey *et al*, 2005). By blending, it can provide chitosan with the desire mechanical strength and chemical stability (Liu and Bai, 2006). Chitosan membranes blended with poly (vinyl alcohol) (PVA) have already been reported to have good mechanical properties because of the

specific intermolecular interactions between PVA and chitosan in the blends (Koyano et al, 1999).

Besides that, degree of acetylation (DA) and molecular mass (MM) of PVA has become most important structural characteristic that determine many of the biopolymer properties which including solubility. DA also effect the permeability of the PVA membrane inversely related to MM of PVA. Concerning the mechanical properties, it has been increase as the DA is decrease. The increase of MM of PVA is generally accepted to increase the mechanical properties (Santod *et al.*, 2006). Anjali *et al* (2006) had revealed that, blending of PVA with CS was to improve the flux by reducing crystallinity without significantly altering the selectivity. Additionally, ionic interaction between PVA and CS could possibly improve the separation by reducing the organic sorption due to 'salting out effect'.

Poly (vinyl alcohol) is hydrophilic and have reactive hydroxyl group. This factor can be modified with other reactive functional groups, amine groups. The amine groups is however much more reactive then the hydroxyl groups and can be used directly as affinity adsorption sites or can be much more easily attacked by other modifying agent under mild condition. Therefore, one of the choices to prepare adsorptive membrane can be to introduce some other amine groups into PVA as the membrane material (Bing *et al*, 2005). More recently, blending PVA with other polymer has been found to be an effective way to overcome the shortcoming of chitosan (Liu and R. Bai., 2005).

The morphology of the polymer blend is often significantly affected by the interaction between the components of the blend that in turn affects also the properties of the blend. Therefore, the major problems to be considered for polymer blend are miscibility (Chuang *et al*. 1999). Therefore, acetic acids are used as a solvent in order to dissolves perfectly the PVA and chitosan during the preparation of dope solution.

1.3 Objectives of Study

Based on the background of this study, the objectives of this study are listed as following:

i. To fabricate high flux chitosan and poly (vinyl alcohol) blend membrane with different concentration of chitosan.
ii. To study the effect of different concentrations of chitosan to membrane performance.
iii. To study the effect of different concentration of chitosan to membrane morphology changes.

1.4 Scope of Study

i. Fabrications of chitosan and PVA blend membrane using acetic acid as solvent and different concentration of chitosan.
ii. Test the performance of chitosan and PVA blend membrane using bovine serum albumin (BSA) and lysozime.
iii. Characterize the membrane using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

CHAPTER 2

LITERATURE REVIEW

2.1 History of Membrane

Two developments can be distinguished as far as the history of membrane technology is concern; which are scientific development and commercial development. Even towards the middle of the eighteen century membrane phenomena were observed and studied, primarily to elucidate the barrier properties and related phenomena rather than to develop membranes for technical and industrial applications (Mulder, 1996).

The period from 1960 to 1980 produced a significant change in the status of membrane technology. Building on the original Loeb–Sourirajan technique, other membrane formation processes, including interfacial polymerization and multilayer composite casting and coating, were developed for making high performance membranes. Using these processes, membranes with selective layers as thin as 0.1μm or less are now being produced by a number of companies (Mulder, 1996). Methods of packaging membranes into large-membrane-area spiral-wound, hollow-fine-fiber, capillary, and plate-and-frame modules were also developed and advances were made in improving membrane stability. By 1980, microfiltration, ultrafiltration, reverse osmosis and electrodialysis were all established processes with large plants installed worldwide (Baker, 2004).

Traditionally, research on membrane has not been carried out solely by chemist and physicist, but also other biochemist, biophysicist and zoologist. Some

scientific milestones worthy on mention are listed in Table 2.1 a number of the authentic contribution listed in that table have been published recently in a special issues of the Journal of Membrane Science the publication of volume 100 (Mulder, 1996).

Table 2.1: Scientific milestones (Mulder, 1996)

Observations	Osmosis: Nollet 1748 Electoosmosis: Reuss 1803, Porret 1816
Relation	Diffusion: Fick 1855 Osmotic pressure: Van ‘t Hoff 1887 Electrolyte transport: Nernst- Planck 1889
Theoretical considerations	Osmotic pressure: Einstein 1905 Membrane potentials: Henderson 1907 Membrane equilibrium: Donnan 1911
Transport models	Ionic membranes: Teorell 1937, Meyer and Sievers 1936 Pore model: Schmid 1950, Meares 1956

Table 2.2 lists the development of some membrane process. The first commercial membranes for practical applications were manufactured by Sartorius in Germany after World War I which originating from the early works of Zsigmondy. However these porous cellulose nitrate or cellulose nitrate and cellulose acetate membranes were only used on a laboratory scale and the same applied to the denser ultrafiltration membranes develop at the same time. (Mulder, 1996).

Table 2.2: Development of (technical) membrane processes (Mulder, 1996)

Membrane process	Country	Year	Application
Microfiltration (MF)	Germany	1920	Laboratory use(bacteria filter)
UIltrafiltration (UF)	Germany	1930	Laboratory use
Hemodialysis	Netherlands	1950	Artificial kidney
Electrodialysis (ED)	USA	1955	Desalination
Reverse osmosis (RO)	USA	1960	Sea water desalination

A breakthrough as far as industrial membrane applications were concerned was achieved by the development of asymmetric membrane by Loeb and Sourirajan. The work of Henis and Tripodi made industrial separation economically feasible. They palace a very thin homogeneous layer of a polymer with high gas permeability on top of an asymmetric membrane, ensuring that the pores in the top layer were filled and that a leak free composite membrane suitable for gas separation was obtained. Although membranes for membrane distillation which are hydrophobic porous membranes have been existence for a time, this process has only been applied on a pilot-plant scale recently (Mulder, 1996).

Pervaporation is another membrane process that has been developed recently. Binning and coworkers tried to commercialize the pervaporation process for industrial used in the late fifties, but despite intensive investigation they were not very success. This process became competitive with other methods of separation due to the development of process like specific composite membrane for the dehydration of organic solvents (Nunes and Peinemann, 2001). The examples listed in Table 2.2 only related to the beginning of the development technical membrane process. The search for new and better membranes is continuing, not only for membrane processes yet to reach the stage of commercialization but also for already existing membrane process

2.2 Definition of Membrane

A general definition of membrane is a selective barrier between two phases. The term of selective is referring to a membrane or a membrane process. The membrane acts as a semipermeable barrier and separation occurs by the membrane controlling the rate of movement of various molecules between two liquid phases, two gas phases or a liquid and a gas phase. The two fluid phases are usually miscible and the membrane barrier prevents actual ordinary hydrodynamic flow (Nicholas, 1998). A membrane can be thick or thin, its structure can be homogeneous or heterogeneous, and transport can be either active or passive. Passive transport can be

driven by a pressure, concentration or a temperature difference. In addition, membrane can be natural or synthetic, neutral or charge.

Membranes can selectively separate components over a wide range of particle sizes and molecular weights, from macromolecular materials such as starch and protein to monovalents ions (William, 2001). Membrane separation processes can be classified into the following groups according to the driving force that cause the flow of permeate through the membrane shown in Table 2.3.

Table 2.3: Classification of membrane processes (Matsuura, 1994)

Type of driving force	Classification of the process
Pressure	Reverse Osmosis Ultrafiltration Microfiltration Membrane gas and vapor separation Pervaporation
Temperature	Membrane distillation
Concentration gradient	Dialysis Membrane extraction
Electric potential	Electrodialysis

The Figure 2.1 is showed that the basic principle of membrane process. Phase 1 is usually considered as the feed or upstream side while phase 2 is considered as permeate or downstream side. Both of the phases could be any combination of miscible or immiscible liquid phases and gaseous phases. Separation occurs due to the ability of membrane to transport one or more selected component from the feed mixture to permeate. The membrane might be thin but does not allow direct contact between the two bulk phases (Lee, 2005).

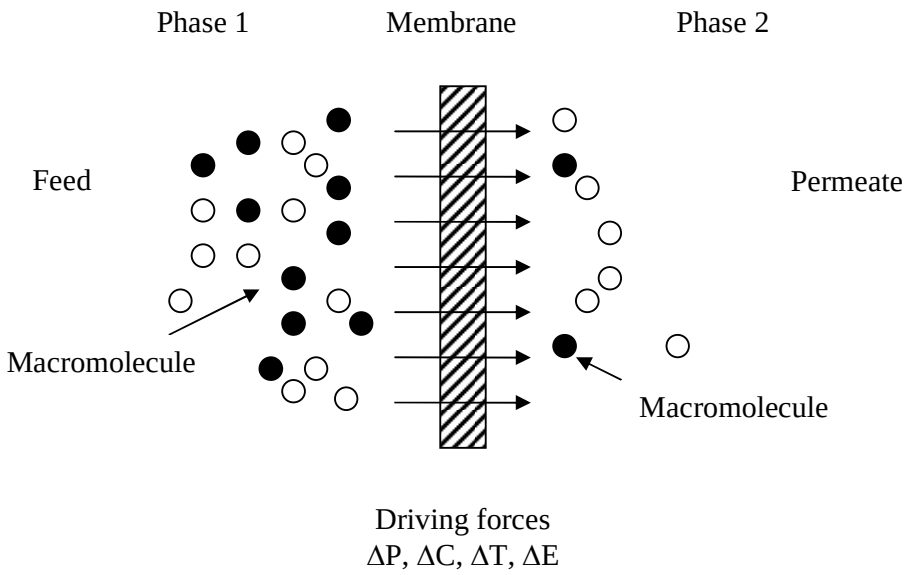

Figure 2.1 The basic principle of membrane process (Lee, 2005)

2.3 Introduction of Membrane Process

In a membrane process, a membrane acts as a selective interphase between two bulk phases (Mulder, 1996). By means of a driving force, some of the species from a multicomponent mixture are transported through the membrane into the other bulk phase while the membranes retain other components. Selective mass transport has occurred. Often a membrane, which has a sufficiently high selectivity, is accompanied by a low transmembrane flux and vice versa making highly selective membrane process too expensive. Membrane separation process enjoys numerous industrial applications such as environmentally benign and it also an appreciable energy savings technique (Baker, 2004),

There are many membrane processes based on different separation principles or mechanisms and specifics problem can cover the broad size range from particles to molecules. In spite of these various differences, all membrane processes have one thing common which is the membrane (Mulder, 1996). The function and

characteristic of the membrane processes such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis, are briefly discussed later in Table 2.4.

Table 2.4: Comparing Four Membrane Process (Rahim, 2006)

	MF	UF	NF	RO
Membrane Types	Symmetrical Asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical
Thickness Thin film	10-150μm	150-250 μm 1 μm	150 μm 1 μm	150 μm 1 μm
Pore size	4-0.02 μm	0.2-0.02 μm	<0.002 μm	<0.002 μm
Rejection	Particles, Clay Bacteria	Macro molecules, Proteins, Polysaccharides vira	High Molecular Weight Cut off (HMWC), Mono-, di-, and oligosaccharides polyvalent negative ions	HMWC, Low Molecular Weight Cut off (LMWC), sodium chloride, glucose
Membrane materials	Ceramic	Ceramic, Thin film	CA Thin film	CA Thin film
Membrane Module	Tubular, hollow fiber	Tubular, hollow fiber, spiral wound, plate and frame	Tubular, spiral wound, plate and frame	Tubular, spiral wound, plate and frame
Operating Pressure	< 2 bar	1-10 bar	5 – 35 bar	15 – 150 bar

a) Microfiltration (MF)

Microfiltration is a pressure-driven process that dynamically separates micron-size or sub-micron particles from the liquid or gaseous feed stream by a membrane (Norihiko *et al*, 1998). Microfiltration membranes have pore sizes in the range 0.1 to 10 μm and thus are typically used to retain bacteria, biological cell